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(54) **Compositions for control of induction system deposits**

Inzufuhranlage für Niederschläge kontrollierende Zusammensetzungen

Compositions pour le contrôle des dépôts dans le système d'admission

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Description

This invention relates to controlling or reducing fuel induction system deposits in internal combustion engines.

A problem frequently encountered in the operation of gasoline and diesel engines is the formation of undesirable amounts of engine deposits, such as induction system deposits, and especially intake valve or injector deposits.

USP 5,006,130 describes reducing intake valve deposits in port fuel injected engines by using a mixture of (a) basic nitrogen in the form of an oil-soluble aliphatic alkylene polyamine containing at least one olefinic polymer chain, said polyamine having a molecular weight of about 600 to about 10,000, and (b) oil-soluble olefinic polymers, poly (oxyalkylene) alcohol, glycol or polyol or mono- or diether thereof, non-aromatic oils or polyalphaolefins.

USP 4,155,718 describes the inhibition or prevention of octane requirement increase in a spark ignited internal combustion engine by introducing with the combustion charge a fuel composition containing an octane requirement increase-inhibiting amount of: (a) certain cyclomatic manganese compounds, (b) certain oil soluble aliphatic polyamines, and (c) oil of lubricating viscosity in certain range of weight ratio of (a): (b): (c).

EP-A-0476196 describes hydrocarbonaceous fuels and additive compositions therefor which comprise: a) one or more fuel-soluble manganese carbonyl compounds; b) one or more fuel-soluble alkali or alkaline earth metal-containing neutral or basic detergent salts; and c) one or more fuel-soluble ashless dispersants. The compositions possess improved combustion characteristics (e.g., formation of less soot, smoke, carbonaceous products and/or noxious emissions), and form on combustion carbonaceous products of reduced acidity.

In accordance with this invention, the effectiveness of certain fuel-soluble induction system deposit control additives is improved by including in a distillate fuel containing one or more such additives, at least one fuel-soluble cyclopentadienyl complex of a transition metal. More particularly, use in distillate fuels of the combination of (i) at least one fuel-soluble detergent/dispersant induction system cleanliness additive described hereinafter, (ii) at least one fuel-soluble cyclopentadienyl complex of a transition metal described hereinafter, and (iii) at least one fuel-soluble liquid carrier or additive inductibility aid described hereinafter can sharply reduce the formation or accumulation of engine deposits such as intake valve deposits in internal combustion engines. In fact, compositions of this invention can function synergistically whereby the effectiveness of a highly effective deposit control additive -- i.e., component (i) above -- can be improved by the addition thereto of the cyclopentadienyl transition metal complex or compound, the latter not known to be a substance that reduces deposits. Additionally, in at least some cases use of the compositions of this invention in gasoline engines can result in control or minimization of octane requirement increase. Moreover, at least some of the compositions of this invention can reduce combustion chamber deposit formation such as deposits which tend to form on piston tops and on cylinder heads. Thus this invention can provide to the art advantages that could not have been foreseen on the basis of any presently-known prior art.

Accordingly, the present invention resides in the use of a fuel composition of a combination of i) at least one fuel-soluble detergent/dispersant selected from (a) fuel-soluble imides of long chain aliphatic hydrocarbon-substituted dicarboxylic acids or their anhydrides, (b) long chain aliphatic hydrocarbons having a polyamine attached directly thereto and (c) Mannich condensation products formed by condensing a long chain aliphatic hydrocarbon-substituted phenol with an aldehyde, and an amine; wherein the long chain hydrocarbon group in (a), (b) and (c) is a polymer of at least one C_2 to C_{10} monoolefin, the polymer having a number average molecular weight of at least about 300; ii) at least one fuel-soluble cyclopentadienyl complex of a transition metal; and iii) at least one fuel-soluble liquid carrier, for controlling intake valve deposits in internal combustion engines operated on gasoline.

Preferably the long chain hydrocarbon group (a), (b) and (c) is a polymer of at least one C_2 to C_5 monoolefin, and most preferably at least one C_3 to C_4 monoolefin, said polymer having a number average molecular weight of at least about 300, preferably at least about 400, and more preferably at least about 700. The type (a) detergent/dispersant is preferably a succinimide of a hydrocarbyl polyamine or a polyoxyalkylene polyamine. The type (b) detergent/dispersant is preferably a - polyisobutenyl polyamine. The type (c) detergent/dispersant is preferably a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight of from 600 to 3000, more preferably in the range of 750 to 1200, (2) an amine, preferably a polyamine, which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, preferably formaldehyde or a formaldehyde-forming reagent or formaldehyde precursor such as a reversible polymer of formaldehyde, wherein the molar ratio of reactants (1):(2):(3) is 1:0.1-10:0.1-10.

The cyclopentadienyl complex or compound is preferably a fuel-soluble cyclopentadienyl iron or manganese compound, most preferably a fuel-soluble cyclopentadienyl manganese tricarbonyl compound. However other fuel-soluble cyclopentadienyl transition metal complexes or compounds can be used.

Deposit formation in the fuel induction system of an internal combustion engine, may be inhibited by providing or using as the fuel for such engine a hydrocarbonaceous distillate fuel, such as a diesel fuel, and preferably a gasoline fuel (including so-called reformulated or oxygenated gasolines) containing the combination of (i), (ii) and (iii) as described above.

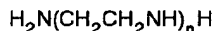
Component (i)

The detergent/dispersant typically has an aliphatic chain (saturated or olefinically unsaturated) which contains an average of at least about 20, preferably at least about 30, and more preferably at least about 50 carbon atoms to provide the fuel solubility and stability required to function effectively as a detergent/dispersant. Typically the long chain aliphatic group will contain as many as 150 or 250 or even more carbon atoms. The long chain aliphatic group of the detergent/dispersant is usually derived from a mixture of aliphatic hydrocarbons such as polypropenes, polybutenes, polyisobutenes, and polyamylenes. The aliphatic chain of the detergent/dispersant is usually a hydrocarbyl group, but it may be a substituted hydrocarbyl group wherein the substituents are certain oxygen-based substituents such as ether oxygen linkages, keto groups (i.e., a carbonyl group bonded to two different carbon atoms), and/or hydroxyl groups.

The detergent/dispersants are typically formed from an aliphatic polyamine although in some cases useful products can be formed from aromatic polyamines. In this connection, the term "aliphatic polyamine" includes both open chain compounds (linear or branched) and ring compounds in which the ring is not aromatic in character. Thus the polyamine can be, for example an open chain polyamine such as diethylene triamine, tris(2-aminoethyl) amine, or hexamethylene diamine, or it can be a nonaromatic cyclic polyamine such as piperazine or N-(2-aminoethyl) piperazine. In addition, the polyamine can be a polyoxyalkylene polyamine such as are available commercially under the Jeffamine trade designation.

Polyamines which may be employed in forming the detergent/dispersant include any that have at least one amino group having at least one active hydrogen atom. A few representative examples include branched-chain alkanes containing two or more primary amino groups such as tetraamino-neopentane; polyaminoalkanols such as 2-(2-aminoethyl-amino)-ethanol and 2-[2-(2-aminoethylamino)-ethylamino]-ethanol; heterocyclic compounds containing two or more amino groups at least one of which is a primary amino group such as 1-(β -aminoethyl)-2-imidazolidone, 2-(2-aminoethylamino)-5-nitropyridine, 3-amino-N-ethylpiperidine, 2-(2-aminoethyl)-pyridine, 5-aminoindole, 3-amino-5-mercaptop-1,2,4-triazole, and 4-(aminomethyl)-piperidine; and the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, N-(2-aminoethyl)-1,3-propanediamine, hexamethylenediamine and tetra-(1,2-propylene)-pentamine.

Preferred amines are the alkylene polyamines, especially the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine, including mixtures thereof in which case n is the average value of the mixture. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, and N,N'-bis(piperaziny)ethane. Typical commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine. Methods for the production of polyalkylene polyamines are known and reported in the literature, e.g., U.S. Pat. No. 4,82737 and references cited therein.

Generally speaking, mixtures of alkylene polyamines such as propylene polyamines and ethylene polyamines suitable for forming the detergent/dispersants will typically contain an average of 1.5 to 10 and preferably an average of 2 to 7 nitrogen atoms per molecule. Ordinarily this reactant will comprise a commercially available mixture. In general, the ethylene polyamine mixtures known commercially as "diethylene triamine" will contain an average in the range of 2.5 to 3.5 nitrogen atoms per molecule. The commercially available ethylene polyamine mixtures known as "triethylene tetramines" will usually contain an average in the range of 3.5 to 4.5 nitrogen atoms per molecule.

Preferred polyamines used in forming the detergent/dispersant for use in middle distillate fuels such as diesel fuel are (1) triethylene tetramine, (2) a combination of ethylene polyamines which approximates triethylene tetramine in overall composition, (3) tetraethylene pentamine, (4) a combination of ethylene polyamines which approximates tetraethylene pentamine in overall composition, (5) pentaethylene hexamine, (6) a combination of ethylene polyamines which approximates pentaethylene hexamine in overall composition, or (7) a combination of any two, any three, any four, any five or all six of (1), (2), (3), (4), (5) and (6). Detergent/dispersants formed from diethylene triamine or mixtures of ethylene polyamines which approximate diethylene triamine in overall composition can also be effectively used in the middle distillate fuels of this invention.

(a) Succinimide Detergent/Dispersants. The preferred succinimide detergent/dispersants for use in gasolines are prepared by a process which comprises reacting (A) an ethylene polyamine selected from (1) diethylene triamine, (2) a combination of ethylene polyamines which approximates diethylene triamine in average overall composition, (3)

triethylene tetramine, (4) a combination of ethylene polyamines which approximates triethylene tetramine in average overall composition, or (5) a mixture of any two or more of (1) through (4), with (B) at least one acyclic hydrocarbyl substituted succinic acylating agent. The substituent of such acylating agent is characterized by containing an average of 50 to 100 (preferably 50 to 90 and more preferably 64 to 80) carbon atoms. Additionally, the acylating agent has an acid number in the range of 0.7 to 1.3 (e.g., in the range of 0.9 to 1.3, or in the range of 0.7 to 1.1), more preferably in the range of 0.8 to 1.0 or in the range of 1.0 to 1.2, and most preferably about 0.9. The detergent/dispersant contains in its molecular structure in chemically combined form an average of from 1.5 to 2.2 (preferably from 1.7 to 1.9 or from 1.9 to 2.1, more preferably from 1.8 to 2.0, and most preferably about 1.8) moles of said acylating agent, (B), per mole of said polyamine, (A).

The acid number of the acyclic hydrocarbyl substituted succinic acylating agent is determined in the customary way --i.e., by titration-- and is reported in terms of mg of KOH per gram of product. It is to be noted that this determination is made on the overall acylating agent with any unreacted olefin polymer (e.g., polyisobutene) present.

The acyclic hydrocarbyl substituent of the detergent/dispersant is preferably an alkyl or alkenyl group having the requisite number of carbon atoms as specified above. Alkenyl substituents derived from poly- α -olefin homopolymers or copolymers of appropriate molecular weight (e.g., propene homopolymers, butene homopolymers, and C_3 and C_4 α -olefin copolymers) are suitable. Most preferably, the substituent is a polyisobutenyl group formed from polyisobutene having a number average molecular weight (as determined by gel permeation chromatography) in the range of 700 to 1200, preferably 900 to 1100, most preferably 940 to 1000. The established manufacturers of such polymeric materials are able to adequately identify the number average molecular weights of their own polymeric materials. Thus in the usual case the nominal number average molecular weight given by the manufacturer of the material can be relied upon with considerable confidence.

The acylating agent for producing the detergent/dispersants is preferably made by reacting a polyolefin of appropriate molecular weight (with or without chlorine) with maleic anhydride. However, similar carboxylic reactants can be employed such as maleic acid, fumaric acid, malic acid, tartaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, ethylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic acid, dimethylmaleic acid, hexylmaleic acid, and the like, including the corresponding acid halides and lower aliphatic esters.

The reaction between the polyamine and the acylating agent is generally conducted at temperatures of 80 °C to 200 °C, more preferably 140 °C to 180 °C, such that a succinimide is formed. These reactions may be conducted in the presence or absence of an ancillary diluent or liquid reaction medium, such as a mineral lubricating oil solvent. If the reaction is conducted in the absence of an ancillary solvent, such is usually added to the reaction product on completion of the reaction. In this way, the final product is more readily handled, stored and blended with other components. Suitable solvent oils include natural and synthetic base oils having a viscosity (ASTM D 445) of preferably 3 to 12 mm²/sec at 100 °C with the primarily paraffinic mineral oils such as a 500 Solvent Neutral oil being particularly preferred. Suitable synthetic diluents include polyesters and hydrogenated or unhydrogenated poly- α -olefins (PAO) such as hydrogenated or unhydrogenated 1-decene oligomer. Blends of mineral oil and synthetic oils are also suitable for this purpose.

As used herein, the term "succinimide" is meant to encompass the completed reaction product from the polyamine and the acylating agent, and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

(b) Aliphatic Polyamine Detergent /Dispersants These detergent/dispersants are known materials prepared by known process technology. One common process involves halogenation of a long chain aliphatic hydrocarbon such as a polymer of ethylene, propylene, butylene, isobutene, amylene, including copolymers such as ethylene-propylene, and butylene-isobutylene, followed by reaction of the resultant halogenated hydrocarbon with a polyamine. If desired, at least some of the product can be converted into an amine salt by treatment with an appropriate quantity of an acid. The products formed by the halogenation route often contain a small amount of residual halogen such as chlorine. Another way of producing suitable aliphatic polyamines involves controlled oxidation (e.g., with air or a peroxide) of a polyolefin such as polyisobutene followed by reaction of the oxidized polyolefin with a polyamine. For synthesis details for preparing such aliphatic polyamine detergent/dispersants, see for example U. S. Pat. Nos. 3,438,757; 3,454,555; 3,485,601; 3,565,804; 3,573,010; 3,574,576; 3,671,511; 3,746,520; 3,756,793; 3,844,958; 3,852,258; 3,864,098; 3,876,704; 3,884,647; 3,898,056; 3,950,426; 3,960,515; 4,022,589; 4,039,300; 4,128,403; 4,166,726; 4,168,242; 5,034,471; 5,086,115; 5,112,364; and 5,124,484; and published European Patent Application 384,086. The long chain substituent(s) of the detergent/dispersant most preferably contain(s) an average of 50 to 350 carbon atoms in the form of alkyl or alkenyl groups (with or without a small residual amount of halogen substitution). Alkenyl substituents derived from poly- α -olefin homopolymers or copolymers of appropriate molecular weight (e.g., propene homopolymers, butene homopolymers, and C_3 and C_4 α -olefin copolymers) are suitable. Most preferably, the substituent is a polyisobutenyl group formed from polyisobutene having a number average molecular weight (as determined by gel permeation chromatography) in the range of 500 to 2000, preferably 600 to 1800, most preferably 700 to 1600.

(c) Mannich Base Detergent/Dispersants While various fuel-soluble long chain Mannich base dispersants formed from a long chain alkylphenol, formaldehyde or a formaldehyde precursor (i.e., a reversible polymer of formaldehyde, also sometimes called a formaldehyde-forming reagent) and a polyamine can be used, the Mannich base detergent/dispersants described in U.S. Pat. No. 4,231,759 are most preferred for use in the practice of this invention.

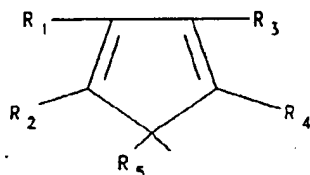
It will of course be understood that if desired, components (a), (b) and/or (c) can be post-treated with various post-treating agents. Technology of this type is well known and extensively reported in the literature.

Component (ii)

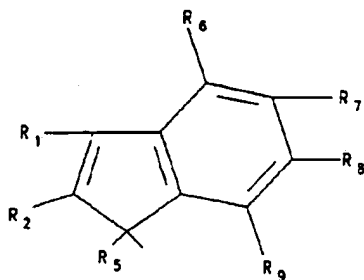
It will be recalled that component (ii) of the compositions of this invention is one or more fuel-soluble cyclopentadienyl complexes (compounds) of a transition metal. Reference herein to "transition metal" means those elements of the periodic system characterized by atoms in which an inner d level of electrons is present but not filled to capacity, namely, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, La, Hf, Ta, W, Re, Os, Ir, Pt, and Ac. From the standpoints of cost, availability and performance, the preferred transition metals for such compounds are those having atomic numbers 22-28, 40, 42, 44, and 74, i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Mo, Ru, and W. Of these, the cyclopentadienyl derivatives of Mn, Fe, Co, and Ni are preferred. Particularly preferred are the fuel-soluble cyclopentadienyl derivatives of iron and manganese. The most preferred component (ii) materials are the cyclopentadienyl manganese tricarbonyl compounds.

The presence of at least one cyclopentadienyl group bonded to an atom of transition metal in the component (ii) transition metal compound is deemed highly important. Without desiring to be bound by theoretical considerations, the existing scientific evidence tends strongly to indicate that a cyclopentadienyl group or moiety forms coordinate covalent bonding with the transition metal atom and thereby confers thermal stability to the resultant compound or complex. For example, in the case of ferrocene and ring-alkyl substituted ferrocenes, it is generally understood that a "sandwich" structure exists wherein an atom of iron is interposed between and covalently coordinated with two cyclopentadienyl and/or alkyl-substituted cyclopentadienyl groups. Besides being fuel soluble, such compounds possess a high degree of thermal stability. A similar situation prevails in the case of cyclopentadienyl manganese tricarbonyl compounds. Here, a manganese atom is covalently coordinated with a cyclopentadienyl or indenyl group or an alkyl-substituted cyclopentadienyl or indenyl group. In addition, three carbonyl groups are bonded to the manganese atom to provide a fuel-soluble, thermally stable organometallic compound having what has been described as a "piano stool" structure.

As used herein, "cyclopentadienyl complex of a transition metal" means a compound ("compound" and "complex" being used interchangeably in this context) in which at least one cyclopentadienyl moiety-containing group is bonded (pi-bonded) to an atom of the transition metal. Other electron-donating groups such as carbonyl, nitrosyl, or hydride can also be bonded to the transition metal compound to provide a compound having suitable fuel solubility, engine inductibility and thermal stability. The cyclopentadienyl moiety-containing group can be depicted as follows:



where each of R_1 , R_2 , R_3 , R_4 , and R_5 is, independently, a hydrogen atom or a hydrocarbyl group (usually but not exclusively, alkyl, alkenyl, cycloalkyl, aryl or aralkyl), and where R_3 and R_4 taken together can form an aryl or hydrocarbyl-substituted aryl group fused onto the cyclopentadienyl group as, for example in the case of an indenyl group:



where each of R_1 , R_2 , R_5 , R_6 , R_7 , R_8 , and R_9 is, independently, a hydrogen atom or a hydrocarbyl group (usually but not exclusively, alkyl, alkenyl, cycloalkyl, aryl or aralkyl).

One preferred type of cyclopentadienyl complex of a transition metal is comprised of compounds of the general formula:



where M is a transition metal, especially iron, cobalt or nickel, and A and B are preferably the same, but can be different from each other, and are hydrocarbyl cyclopentadienyl moiety-containing groups which have from 5 to about 24 carbon atoms, and more preferably from 5 to 10 carbon atoms each. A few illustrative examples include biscyclopentadienyl iron, (i.e., ferrocene), cyclopentadienyl methylcyclopentadienyl iron (i.e., monomethyl ferrocene), bis(methylcyclopentadienyl) iron (i.e., ferrocene in which both rings each has a methyl substituent), cyclopentadienyl ethylcyclopentadienyl iron, bis(ethylcyclopentadienyl) iron, bis(di-methylcyclopentadienyl) iron, bis(trimethylcyclopentadienyl) iron, cyclopentadienyl tert-butylcyclopentadienyl iron, bis(pentamethylcyclopentadienyl) iron, methylcyclopentadienyl ethylcyclopentadienyl iron, bis(hexylcyclopentadienyl) iron, bisindenyl iron, biscyclopentadienyl nickel (i.e., nickelocene), cyclopentadienyl methylcyclopentadienyl nickel, bis(methylcyclopentadienyl) nickel bis(isopropylcyclopentadienyl) nickel, bisindenyl nickel, biscyclopentadienyl cobalt, bis(methylcyclopentadienyl) cobalt, and bis(dimethylcyclopentadienyl) cobalt. Of these compounds, ferrocene and monoalkyl- and dialkyl-substituted ferrocenes (each alkyl group having up to 6 carbon atoms) are more preferred, with ferrocene and the methylferrocenes being most preferred.

Another preferred type of cyclopentadienyl complex of a transition metal is composed of compounds of the general formula:



where A is a cyclopentadienyl group such as depicted above in formulas (II) and (III) and having from 5 to 24 carbon atoms and more preferably from 5 to 10 carbon atoms; M is a transition metal, especially manganese, iron, cobalt, and nickel; C and D are electron donating groups (such as carbonyl, nitrosyl, hydride, hydrocarbyl, nitrilo, amino, trihydrocarbylamino, trihaloamino, trihydrocarbyl phosphite, trihalophosphine, and 1,3-diene); z is a whole integer from 1 to 2; x is a whole integer from 1 to 4, and y is a whole integer from 0 to 4, and where C and D, when both are present, differ from each other and the sum of the electrons donated by C (and D when present) when added to 5 being equal to the atomic number of an inert gas whose atomic number is above, but closest to, the atomic number of the transition metal, M. Note in this connection, U.S. Pat. No. 2,818,416.

Illustrative examples of such cyclopentadienyl complexes of a transition metal are cyclopentadienyl manganese benzene; methylcyclopentadienyl manganese (dicarbonyl) (tetrahydrofuran); methylcyclopentadienyl manganese (dicarbonyl) (methyltetrahydrofuran); methylcyclopentadienyl manganese (dicarbonyl) (tin dichloride); methylcyclopentadienyl manganese (dicarbonyl) (acetylacetonate); cyclopentadienyl manganese (dicarbonyl) (4-vinylpyridine); methylcyclopentadienyl manganese (dicarbonyl) (4-vinylpyridine); cyclopentadienyl manganese (dicarbonyl) (triphenylphosphine); methylcyclopentadienyl manganese (dicarbonyl) (triphenylphosphine); cyclopentadienyl manganese (carbonyl) di(tetrahydrofuran); methylcyclopentadienyl manganese (dicarbonyl) (alkanol) where the alkanol is methanol or ethanol or mixtures thereof; cyclopentadienyl iron (dicarbonyl) (iodide); cyclopentadienyl iron (carbonyl) (iodide) (methyltetrahydrofuran); cyclopentadienyl cobalt dicarbonyl; cyclopentadienyl nickel nitrosyl, and methylcyclopentadienyl nickel nitrosyl.

The most preferred component (ii) compounds are the cyclopentadienyl manganese tricarbonyl compounds such as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, and indenyl manganese tricarbonyl, including mixtures of two or more such compounds. Preferred are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, and mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl.

Component (iii)

As pointed out above, the compositions of this invention also contain a carrier fluid (also known as a solvent, diluent, or induction aid). Useful as carrier fluids or induction aids are such materials as liquid poly- α -olefin oligomers, liquid polyalkene hydrocarbons (e.g., polypropene, polybutene, or polyisobutene), liquid hydrotreated polyalkene hydrocarbons (e.g., hydrotreated polypropene, hydrotreated polybutene, or hydrotreated polyisobutene), mineral oils, liquid polyoxyalkylene compounds, liquid alcohols or polyols, liquid esters, and similar liquid carriers or solvents. Mixtures of two or more such carriers or solvents can be employed.

In the practice of this invention particular types of carrier fluids are especially preferred because of their performance capabilities, but others can also be used. The preferred carrier fluids are 1) one or a blend of mineral oils having a viscosity index of less than about 90 and a volatility of 50% or less as determined by the test method described below, 2) one or a blend of poly- α -olefins having a volatility of 50% or less as determined by the test method described below, 3) one or more polyoxyalkylene compounds having an average molecular weight of greater than about 1500, 4) a paraffinic base mineral oil having a viscosity of 65 cSt (300 SUS) at 40°C to 150 cSt (700 SUS) at 40°C, or 5) a mixture of any two or all four of 1), 2), 3) and 4). Preferred are blends of 1) and 2), and blends of 1) and 3).

The test method used for determination of volatility in connection with the carrier fluids of 1) and 2) above is as follows: Mineral oil or poly- α -olefin (110-135 grams) is placed in a three-neck, 250 mL round-bottomed flask having a threaded port for a thermometer. Such a flask is available from Ace Glass (Catalog No. 6954-72 with 20/40 fittings). Through the center nozzle of the flask is inserted a stirrer rod having a Teflon blade, 19 mm wide x 60 mm long (Ace Glass catalog No. 8085-07). The mineral oil is heated in an oil bath to 300°C for 1 hour while stirring the oil in the flask at a rate of 150 rpm. During the heating and stirring, the free space above the oil in the flask is swept with 7.5 L/hr of air or inert gas (e.g., nitrogen, or argon,). The volatility of the fluid thus determined is expressed in terms of the weight percent of material lost based on the total initial weight of material tested.

As noted above, one type of preferred carrier fluid is one or a blend of mineral oils having a viscosity index of less than about 90 and a volatility of 50% or less as determined by the test method described above. Mineral oils having such volatilities that can be used include naphthenic and asphaltic oils.

Another preferred type of carrier fluid is one or a blend of paraffinic mineral oils of suitable viscosity range, typically in the range of 65 cSt (300 SUS) at 40°C to 150 cSt (700 SUS) at 40°C, and preferably in the range of 100 cSt (475 SUS) at 40°C to 135 cSt (625 SUS) at 40°C. Such oils can be processed by standard refining procedures such as solvent refining. Thus, effective use can be made of paraffinic base solvent neutral mineral oils in the range of 350N to 700N and preferably in the range of 500N to 600N.

The poly- α -olefins (PAO) which are included among the preferred carrier fluids of this invention are the hydrotreated and unhydrotreated poly- α -olefin oligomers, i.e., hydrogenated or unhydrogenated products, primarily trimers, tetramers and pentamers of α -olefin monomers, which monomers contain from 6 to 12, generally 8 to 12 and most preferably about 10 carbon atoms. Their synthesis is outlined in Hydrocarbon Processing, Feb. 1982, page 75 et seq. and is described in the patents cited hereinafter in this para-graph. Typically, the poly- α -olefins used have a viscosity (measured at 100°C) in the range of 2 to 20 centistokes (cSt). Preferably, the poly- α -olefin has a viscosity of at least 8 cSt, and most preferably about 10 cSt at 100°C. The hydrotreated poly- α -olefin oligomers are readily formed by hydrogenating poly- α -olefin oligomers using conditions such as are described in U.S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822.

The polyoxyalkylene compounds which are among the preferred carrier fluids for use in this invention are fuel-soluble compounds which can be represented by the following formula



wherein R_1 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, R_2 is an alkylene group having 2-10 carbon atoms (preferably 2-4 carbon atoms), R_3 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, and n is an integer from 1 to 500 representing the number of repeating alkoxy groups. Preferred polyoxyalkylene compounds are comprised of repeating units formed by reacting an alcohol with an alkylene oxide wherein the alcohol and alkylene oxide contain the same number of carbon atoms.

One useful sub-group of polyoxyalkylene compounds is comprised of the hydrocarbyl-terminated poly(oxyalkylene) monools such as are referred to in the passage at column 6, line 20 to column 7 line 14 of U.S. Pat. No. 4,877,416 and references cited in that passage. A most preferred sub-group of polyoxyalkylene compounds is made up of compounds of formula IV above wherein the repeating units are comprised substantially of C_3H_6-O , and wherein R_1 is a

hydroxy group and R_3 is a hydrogen atom. Polyoxyalkylene compounds useful for this invention which are commercially available include Polyglycol P-1200, Polyglycol L1150, and Polyglycol P-400, which are available from the Dow Chemical Company.

The average molecular weight of the polyoxyalkylene compounds used as carrier fluids is preferably in the range of from 200 to 5000, more preferably from 1000 to 4500, and most preferably from above 1500 to 4000. For purposes of this invention, the end groups, R_1 and R_3 , are not critical as long as the overall polyoxyalkylene compound is sufficiently soluble in the fuel compositions and additive concentrates of this invention at the desired concentration to provide homogeneous solutions that do not separate at low temperatures such as -20°C .

Another group of preferred carriers is the liquid polyalkylenes such as polypropenes, polybutenes, polyisobutenes, polyamylenes, copolymers of propene and butene, copolymers of butene and isobutene, copolymers of propene and isobutene, and copolymers of propene, butene and isobutene. Use of materials of this general type together with other carrier fluids is described for example, in U.S. Pat. Nos. 5,089,028 and 5,114,435.

Proportions

The proportion of the cyclopentadienyl metal complex or compound such as a ferrocene compound or a cyclopentadienyl manganese tricarbonyl compound used in the compositions of this invention is such that the resultant composition when consumed in an engine results in improved intake valve cleanliness as compared intake valve cleanliness of the same engine operated on the same composition except for being devoid of cyclopentadienyl metal compound. Thus in general, the weight ratio of detergent/dispersant to metal in the form of cyclopentadienyl metal compound will usually fall within the range of 3 : 1 to 100 : 1, and preferably within the range of 6 : 1 to 50 : 1. For the purpose of ascertaining these ratios, the weight of the detergent/dispersant is the weight of the product as produced including unreacted polyolefin associated with the product as produced together with process diluent oil, if any, used during the production process to facilitate the reaction, but excluding the weight of any additional diluent that may be added to the detergent/dispersant after it has been produced, and of course excluding the weight of the carrier fluid component (iii).

Typically the additive compositions of this invention contain from 5 to 50 wt %, and preferably from 10 to 25 wt % of the long chain active detergent/dispersant and from 1 to 15 wt %, and preferably from 3 to 10 wt % of cyclopentadienyl transition metal compound with the balance of the composition consisting essentially of the liquid carrier, diluent, solvent, or induction aid (however it be named). Here again, the weight of the detergent/dispersant is the weight of the product as produced including unreacted polyolefin associated with the product as produced, if any, together with process diluent oil, if any, used during the production process to facilitate the reaction, but excluding the weight of any additional diluent that may be added to the detergent/dispersant after it has been produced. If desired, these compositions may contain small amounts (e.g., a total of up to about 10 wt % and preferably a total of up to about 5 wt % based on the total weight of the additive composition), of one or more fuel-soluble antioxidants, demulsifying agents, rust or corrosion inhibitors, metal deactivators, or marker dyes.

When formulating the fuel compositions of this invention, the additives are employed in amounts sufficient to reduce or inhibit deposit formation in an internal combustion engine. Thus the fuels will contain minor amounts of the above additives (i), (ii) and (iii) -- i.e., detergent/dispersant, cyclopentadienyl transition metal compound, carrier fluid -- that control or reduce formation of engine deposits, especially intake system deposits, and most especially intake valve deposits in spark-ignition internal combustion engines. Generally speaking the fuels of this invention will contain an amount of the detergent/dispersant, component (i), in the range of 20 to 500 ppm, and preferably in the range of 100 to 400 ppm; an amount of transition metal in the form of a cyclopentadienyl transition metal complex or compound, component (ii), in the range of 2.061×10^{-3} to 6.60×10^{-2} g/l of transition metal (0.0078 to 0.25 gram per gallon), and preferably in the range of 4.12×10^{-3} to 3.30×10^{-2} g/l of transition metal (0.0156 to 0.125 gram per gallon); and an amount of carrier fluid, component (iii), in the range of 20 to 2000 ppm, and preferably in the range of 100 to 1200 ppm.

The optimum proportions of the carrier fluid used depend to some extent on the identity of the carrier fluid. When using mineral oil fluids or poly- α -olefin carrier fluids (hydrotreated or unhydrotreated) or mixtures of the mineral oil fluids and the PAO, the amount of carrier fluid will preferably correspond to a weight ratio of detergent/dispersant to carrier fluid in the range of 0.3 : 1 to 1 : 1. When using one or more polyoxyalkylene compounds either alone or in admixture with a mineral oil carrier, the amount of carrier fluid preferably corresponds to a weight ratio of the detergent/dispersant to the carrier fluid falling in the range of 0.05 : 1 to 0.5 : 1. When using a combination of the mineral oil, the unhydrotreated poly- α -olefin and the polyoxyalkylene compound, the carrier fluid is preferably proportioned to yield a weight ratio of the detergent/dispersant to the total carrier fluid falling in the range of 0.25 : 1 to 1 : 1. It is to be noted that the foregoing proportions are based on the weight of the detergent/dispersant as produced (including unreacted polyolefin associated with the product as produced together with process diluent oil, if any, used during the production process to facilitate the reaction. However the weight of the detergent/dispersant does not include the weight of any additional diluent that may be added to the detergent/dispersant after it has been produced. Thus if using a purchased

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intake valve deposit control additive package which contains a suitable carrier fluid the dosage used should take into consideration the fact that such products typically do contain a carrier fluid.

When a mixture of any two or all four types of the preferred carrier fluids is used, the proportions of the respective types of carrier fluids can vary over the entire range of relative proportions. For best results, however, the following proportions on a weight basis are recommended when using mixtures of two such carrier fluids:

- For a mixture of 1) mineral oil and 2) hydrotreated or unhydrotreated poly- α -olefin, the weight ratio of 1) to 2) is preferably in the range of 0.5 : 1 to 3 : 1.
- For a mixture of 1) mineral oil and 3) polyoxyalkylene compound, the weight ratio of 1) to 3) is preferably in the range of 4 : 1 to 7 : 1.
- For a mixture of 2) hydrotreated or unhydrotreated poly- α -olefin and 3) polyoxyalkylene compound, the weight ratio of 2) to 3) is preferably in the range of 0.25 : 1 to 4 : 1.

The additives used in formulating the fuels of this invention can be blended into the base fuel individually or in various sub- combinations.

The surprising properties manifested by compositions of this invention were demonstrated by actual road tests conducted using a BMW 318i vehicle operated on a group of four test fuels. The base fuel used throughout this group of tests was Phillips J fuel. This fuel contains no detergent/dispersant and no added metal-containing compound. The vehicle was operated under the same conditions with new intake valves at the start of each test. After known mileage accumulation with a given test fuel, the intake valves were removed from the engine and the weight of the valve deposits was determined and averaged for the four intake valves. The four fuels tested in this manner were as follows:

- Fuel A - Base fuel as received
- Fuel B - Base fuel containing 0,715 kg/m³ (250 pounds per thousand barrels (ptb)) of an additive composition of Example 4 hereinafter except that the methylcyclopentadienyl manganese tricarbonyl was omitted
- Fuel C - Base fuel containing 0.00825 g/l (0.03125 (i.e., 1/32) g/gal) of manganese as methylcyclopentadienyl manganese tricarbonyl
- Fuel D - Base fuel containing 0.715 kg/m³ (250 ptb) of the additive composition used in Fuel B, and 0.00825 g/l (0.03125 g/gal) of manganese as methylcyclopentadienyl manganese tricarbonyl.

Table I summarizes the results of these tests, and Table II sets forth the inspection data of the base fuel used in these tests.

Table I

Fuel Used	Kilometres (Miles) of Operation	Average Intake Valve Weight, mg
Fuel A	6,925 (4,300)	100
Fuel B	16,100 (10,000)	42
Fuel C	8,050 (5,000)	120
Fuel D	16,100 (10,000)	5

Table II

Test Description	Final Result	ASTM Test Method
Distillation, Gasoline, °C (°F)		D86
Initial Boiling Temperature	30 (86)	
05% Evaporated Temperature	42 (107)	
10% Evaporated Temperature	51 (124)	
20% Evaporated Temperature	60 (140)	
30% Evaporated Temperature	71 (159)	
40% Evaporated Temperature	86 (187)	
50% Evaporated Temperature	103 (217)	
60% Evaporated Temperature	114 (237)	
70% Evaporated Temperature	124 (256)	

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Table II (continued)

Test Description	Final Result	ASTM Test Method
80% Evaporated Temperature	140 (284)	
90% Evaporated Temperature	165 (329)	
95% Evaporated Temperature	189 (368)	
End Point	222 (432)	
% Overhead Recovery	97.4	
% Residue	1.0	
% Loss	1.6	
Potential Gum Content, mg		D873; D381
Potential Residue, Precipitate	<0.1	
Potential Residue, Insoluble Gum	147.4	
Potential Gum, Soluble Gum	7.2	
Potential Gum, Total Gum	154.6	
Acid Number, Total, mg KOH/g	<0.1	D664
Peroxides, Organic Assay, %/peroxide number	<0.01	E 298-84
Gravity, ° API - 60/60F	54.8	D287
Oxidation Stability, minutes	1440	D525
Total Sulfur, ppm wt.	199	D3120
Reid Vapor Pressure, Pa(PSI)	0.50 (7.4)	D323
Water, Karl Fischer Titration, ppm	292	D1744
Gum Content, Washed, mg/100mL	0.4	D381
Gum Content Unwashed, mg/100mL	2.0	D381
Lead Content, g/l (g/gal)	< 0.0003 (< 0.001)	D3237

In view of the astonishing results described in Table I above, additional tests were performed in a different BMW 318i fuel-injected vehicle. In these tests Fuel E corresponded to Fuel B above except that the additive composition was used at the level of 0.572 kg/m³ (200 ptb) rather than 0.715 kg/m³ (250 ptb). In Fuel F, which was representative of the compositions of this invention, the base fuel contained 0.572 kg/m³ (200 ptb) of the additive composition used in Fuel B, and 0.00825 g/l (0.03125 g/gal) of manganese as methylcyclopentadienyl manganese tricarbonyl. Results from these tests at 8,050 and 16,100 km (5000 and 10,000 miles) are summarized in Table III.

Table III

Fuel Used	Kilometres (Miles) of Operation	Average Intake Valve Weight, mg
Fuel E	8,050 (5,000)	60
Fuel E	16,100 (10,000)	95
Fuel F	8,050 (5,000)	18
Fuel F	16,100 (10,000)	16

In another pair of tests using the above test procedure and the same base fuel, a comparison was made as between base fuel containing 0.572 kg/m³ (200 ptb) a commercially-available polyisobutenyl polyamine composition (Fuel G) and the base fuel containing 0.572 kg/m³ (200 ptb) of the same commercially-available polyisobutenyl polyamine com-

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position plus 0.00825 g/l (0.03125 g/gal) of manganese as methylcyclopentadienyl manganese tricarbonyl (Fuel H). Based on analyses of the polyisobutenyl polyamine composition, Fuels G and H contained approximately 0.126 kg/m³ (44 ptb) of the active polyisobutenyl-polyamine detergent/dispersant and approximately 0.446 kg/m³ (156 ptb) of carrier fluid and solvent. Results from these tests at 8,050 km (5000 miles) are summarized in Table IV. For ease of reference, the results on the same base fuel without additives (Fuel A) and the same base fuel containing 0.00825 g/l (0.03125 g/gal) of manganese as methylcyclopentadienyl manganese tricarbonyl (Fuel C) are also presented in Table IV.

Table IV

Fuel Used	Kilometres (Miles) of Operation	Average Intake Valve Weight, mg
Fuel A	6,925 (4,300)	100
Fuel C	8,050 (5,000)	120
Fuel G	8,050 (5,000)	38
Fuel H	8,050 (5,000)	0

Another group of tests was conducted using a different commercially-available long chain succinimide-based detergent/dispersant composition (HiTEC® 4450 additive) with and without addition of 6.4 ppm of manganese as methylcyclopentadienyl manganese tricarbonyl. In these tests, the base fuel had the characteristics set forth in Table V.

Table V

Test Description	Final Result
Hydrocarbon Composition, Volume %	
Aromatics	36.6
Olefins	6.3
Saturates	57.1
Disillation, Gasoline, °C	
Initial Boiling Temperature	31
10% Evaporated Temperature	51
50% Evaporated Temperature	104
90% Evaporated Temperature	161
End Point	205
% Overhead Recovery	99
Specific Gravity	0.7574
Total Sulfur, wt %	0.04 max
Reid Vapor Pressure, Pa (PSI)	0.622 (9.14)
Gum Content, Washed, mg/100mL	0.4
Research Octane Number (RON)	95 min
Motor Octane Number (MON)	85 min
(RON + MON)/2	90 min

The test procedure used in this series of tests was the Mercedes-Benz M 102 E Inlet Valve Cleanliness Test. This

is an engine dynamometer test which utilizes a Mercedes-Benz 102 2.3 liter engine with Bosch KE-Jetronic fuel injection. The engine is operated for 60 hours under cycling conditions, with the intake valves pegged to prevent rotation. The test cycle is broken into four operating segments, with a total cycle time of 4.5 minutes. The four stages are shown in Table VI.

TABLE VI

STAGE	TIME, min	SPEED, rpm	TORQUE, Nm	POWER, Kw
1	0.5	800	0	0
2	1.0	1300	29.4	4
3	2.0	1850	32.5	6.3
4	1.0	3000	35.0	11.0

Before beginning a test, intake ports and combustion chambers are cleaned of any deposits. Spark plugs are checked and replaced if necessary, and fuel injectors are checked for proper fuel delivery. Cleaned, pre-weighed intake valves are installed in the head using new valve stem seals. Intake valve guides are monitored for wear and replaced when necessary. The engine is charged with 3.7 kg of CEC-RL 140 Reference Oil. When the test is in its last hour of operation, blow-by is measured at the conditions of Stage 4. Blow-by cannot exceed 20 liters per minute.

Once the test has concluded, the intake valves are removed from the engine. Deposits on the combustion chamber side of the valves are cleaned, the intake valve is submerged in n-heptane for 10 seconds, and then shaken dry. After 10 minutes of drying, the intake valves are weighed, and the weight increase due to deposits is recorded. In these tests, a visual rating of the valves was performed using the CRC Valve Rating Scale.

Table VII summarizes the results of this series of tests. Fuel I is the above base fuel. Fuel J is the above base fuel containing 0.729 kg/m³ (255 ptb) of the succinimide based detergent/dispersant composition (HiTEC® 4450 additive; Ethyl Petroleum Additives, Inc.). Fuel K is a fuel of this invention in that it contains both the foregoing succinimide based detergent/dispersant 0.715 kg/m³ (250 ptb) and 6.4 ppm of manganese as methylcyclopentadienyl manganese tricarbonyl. Fuels J and K both contained paraffinic mineral oil carrier fluid and active succinimide detergent in a weight ratio of approximately 3.3 : 1, respectively.

TABLE VII

FUEL	INTAKE VALVE DEPOSIT WEIGHT, mg					CRC VALVE RATING
	VALVE 1	VALVE 2	VALVE 3	VALVE 4	VALVE AVERAGE	
I	272	341	565	309	372	7.5
J	6	108	14	114	61	8.8
K	10	31	11	46	24	9.4

In a paper entitled "Particulate Emissions from Current Model Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl" by R. H. Hammerle, T. J. Korniski, J. E. Weir, E. Chladek, C. A. Gierczak and R. G. Hurley of the Ford Motor Company (SAE Technical Paper No. 912436), and in a paper entitled "The Effect on Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT) by R. G. Hurley, L. A. Hansen, D. L. Guttridge, H. S. Gandhi, R. H. Hammerle and A. D. Matzo of the Ford Motor Company (SAE Technical Paper No. 912437), references are made to tests conducted using an unleaded gasoline containing MMT and Chevron's patented Techroline gasoline additive in the concentration used in their commercial gasolines. This Chevron additive (available commercially as Chevron OGA-480 additive) is a carbamate detergent/dispersant-based composition containing polyether and amine groups joined by a carbamate linkage.

Inasmuch as this test fuel used by Ford is deemed to be the closest composition not of this invention to the gasoline compositions of this invention, tests were conducted to compare the effectiveness of this Ford combination of detergent/dispersant and a cyclopentadienyl complex of a transition metal with the effectiveness of two different fuel compositions of this invention. In a series of such tests, comparative performance was determined using a Ford 2.3 Liter Intake Valve Deposit Test.

This 2.3 Liter Ford Test uses a 1985 2.3 Liter Ford engine cycled between high idle and moderate load conditions. The operating conditions are shown in Table VIII. The total time for each 2-stage cycle is 4 minutes. During the test, the engine coolant-out temperature is controlled to 74 ± 3°C (165 ± 5°F). A typical mid-continent regular unleaded gasoline was used as the base fuel.

TABLE VIII

EVENT	DURATION	RPM	HP
Power	3 min.	2800	36-38
Idle	1 min.	3000	0-4

The test engine is assembled to manufacturer's specifications. Each test begins with new, pre-weighed intake valves. New exhaust valves are installed every fourth test. Valve seals are replaced each test. Fuel and air delivery systems are cleaned and rated. Spark plugs are replaced, injectors are checked for the proper fuel flow rate, and the engine is charged with fresh 10W40 oil.

After 112 hours of cycling, the intake valves are removed from the engine. Deposits are removed from the intake valve face and seal ridge. The valves are rinsed with hexane, dried in a 93.3°C (200°F) oven, and stored in a desiccator until they are weighed and rated. These tests were conducted consecutively under the above test conditions in the same Ford 2.3 liter engine with the same cylinder head and with the same batch of base fuel (Union Oil Company clear -- i.e., additive-free -- gasoline). Table IX summarizes the additive compositions and the test results in these 2.3 Liter Ford Intake Valve Deposit Tests. In Table IX, additive A is a long-chain Mannich base intake valve deposit control composition in which the Mannich base dispersant was Amoco 597 additive. The composition was composed of equal parts by weight of Amoco 597 additive and a 600 neutral paraffinic oil carrier fluid. Small, conventional amounts of other conventional additives (rust inhibitor or demulsifying agent) were present in Additive A. Additive B was the commercially available carbamate-based detergent/dispersant composition (Chevron OGA-480 additive). Additive C was a succinimide-based detergent/dispersant composition (HiTEC® 4403 additive; Ethyl Petroleum Additives, Inc.). The fuels treated with Additive C contained approximately two parts by weight of a mineral oil carrier fluid per part by weight of the active succinimide detergent/dispersant.

Table IX summarizes the results of these comparative tests.

TABLE IX

TEST NUMBER	ADDITIVE	CONCENTRATION, kg/m ³ (pounds per thousand barrels)	MMT, 0.00825g/l (1/32 g Mn Per Gallon)	INTAKE VALVE DEPOSIT WEIGHT, mg				
				Valve 1	Valve 2	Valve 3	Valve 4	Valve Average
157	A	0.618 (216)	No	74	89	58	119	85
158	A	0.618 (216)	Yes	47	42	39	48	44
159	B	0.286 (100)	No	119	138	135	62	114
160	B	0.286 (100)	Yes	83	110	100	73	92
161	C	0.429 (150)	Yes	49	66	48	15	44
162	C	0.429 (150)	No	82	111	133	45	93

It will be seen from the data in Table IX that the addition of MMT to the succinimide and Mannich base additive compositions pursuant to this invention resulted in reductions in total intake valve deposits of 53% and 48%, respectively. On the other hand, the reduction was only 19% when the MMT was added to the polyether polyamine carbamate

deposit control additive composition.

In other Ford 2.3 Liter Intake Valve Deposit Tests conducted in the same manner as above and using the same base fuel, the results summarized in Table X were obtained. In Table X Fuel L was the additive-free Mid-Continent base fuel. Fuel M was the same base fuel containing 0.00825 g/l of manganese (1/32g per gallon) as methylcyclopentadienyl manganese tricarbonyl. Fuel N was the same base fuel containing HiTEC® 4403 additive at a concentration of 0.572 kg/m³ (200 ptb). Fuel O was the same base fuel but which contained 0.00825 g/l of manganese (1/32 gram per gallon) as methylcyclopentadienyl manganese tricarbonyl, and and HiTEC® 4403 additive at a concentration of 0.572 kg/m³ (200 ptb). Fuels N and O contained approximately two parts by weight of a mineral oil carrier fluid per part by weight of the active succinimide detergent/dispersant.

TABLE X

FUEL	INTAKE VALVE DEPOSIT WEIGHT, mg					CRC VALVE RATING
	VALVE 1	VALVE 2	VALVE 3	VALVE 4	VALVE AVERAGE	
L	424	182	429	526	390	8.3
M	89	174	316	184	191	8.8
N	111	93	31	7	61	9.2
O	5	36	8	6	13	9.7

In the foregoing Ford 2.3 Liter Tests, it was found that use of the additive combinations of this invention caused significant reductions in the weight of combustion chamber deposits formed during the tests as compared to the tests wherein the methylcyclopentadienyl manganese tricarbonyl was not used with the detergent/dispersant composition.

Octane requirements were determined at the beginning, middle and end of each Ford 2.3 Liter Test. In each case, the octane requirement increases were lower for the fuels containing the additive combinations of this invention as compared to the octane requirement increases which occurred with the fuels containing only the detergent/dispersant composition.

As noted above, this invention provides in one of its embodiments a fuel additive concentrate comprising the above-specified fuel-soluble detergent/dispersant, a fuel-soluble cyclopentadienyl manganese tricarbonyl compound, and a fuel-soluble liquid carrier or induction aid. Liquid hydrocarbonaceous fuels containing such additive components constitute another embodiment of this invention. In this connection, the term "hydrocarbonaceous fuel" designates not only a blend or mixture of hydrocarbons commonly referred to as gasoline or diesel fuel, but additionally so-called oxygenated fuels (i.e., fuels with which have been blended ethers, alcohols and/or other oxygen-containing fuel blending components as are used in reformulated gasolines). Fuels containing MTBE (methyl tertiary-butyl ether) are preferred oxygenated fuels.

Another embodiment of this invention is a method of controlling intake valve deposits in internal combustion engines operated on gasoline, which method comprises producing and/or providing and/or using as the fuel therefor, a fuel composition as described in the immediately preceding paragraph.

The following Examples in which all parts are by weight illustrate, but are not intended to limit, this invention.

EXAMPLE 1

A fuel additive concentrate is prepared from the following ingredients:

- A) 50 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride having an acid number of 1.1 (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 950) with a commercial mixture approximating triethylene tetramine, in a mole ratio of 2:1 respectively.
- B1) 75 parts of naphthenic mineral oil of Witco Corporation H-4053.
- B2) 25 parts of 10 cSt unhydrotreated PAO formed by oligomerization of 1-decene.
- C) 11.6 parts of methylcyclopentadienyl manganese tricarbonyl
- D) 3.5 parts of a demulsifier mixture composed of alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins in alkylbenzenes (TOLAD® 9308).
- E) 2 parts percent of tetrapropenyl succinic acid supplied as a 50% solution in light mineral oil.

This concentrate is blended with gasolines and with diesel fuels at concentrations of 0.443 kg/m³ (155 pounds per thousand barrels (ptb)).

EXAMPLE 2

A fuel additive concentrate is prepared using components A), B1), B2) and C) as described in Example 1 in the following proportions: 60 parts of A); 60-80 parts of B1); 40-60 parts of B2); and 14 parts of C). In addition, 4 parts of a tertiary butylated phenol antioxidant mixture containing a minimum of 75 percent of 2,6-di-tert-butylphenol, 10-15 percent of 2,4,6-tri-tert-butyl-phenol, and 15-10 percent of 2-tert-butylphenol; 3 parts of Tolad® 286; and 2 parts of tetrapropenyl succinic acid supplied as a 50% solution in light mineral oil are included in the product. This mixture is then blended with gasoline at a rate of 0.515 kg/m³ (180 pounds per thousand barrels (ptb)).

EXAMPLE 3

A fuel additive concentrate is prepared using components A), B1), B2) and C) as described in Example 1 in the following proportions: 75 parts of A); 75-100 parts of B1); 75 parts of B2) and 17.5 parts of C) are used. In addition, 5 parts of a tertiary butylated phenol antioxidant mixture containing a minimum of 75 percent of 2,6-di-tert-butylphenol, 10-15 percent of 2,4,6-tri-tert-butyl-phenol, and 15-10 percent of 2-tert-butylphenol; 3.5 parts of Tolad® 9308; and 2 parts of tetrapropenyl succinic acid supplied as a 50% solution in light mineral oil are included in the finished concentrate. This product mixture is then blended with gasoline at a rate of 0.644 - 0.715 kg/m³ (225-250 pounds per thousand barrels (ptb)).

EXAMPLE 4

A fuel additive concentrate is prepared from the following ingredients:

A) 30 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride having an acid number of 1.1 (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 950) with a commercial mixture approximating triethylene tetramine, in a mole ratio of 1.8 : 1 respectively.

B) 60 parts of naphthenic mineral oil (Exxon 900 solvent neutral pale oil).

C) 7 parts of methylcyclopentadienyl manganese tricarbonyl.

D) 2.8 parts of a tertiary butylated phenol antioxidant mixture containing a minimum of 75 percent of 2,6-di-tert-butylphenol, 10-15 percent of 2,4,6-tri-tert-butylphenol, and 15-10 percent of 2-tert-butylphenol (ETHYL® antioxidant 733, Ethyl Corporation).

E) 1.5 parts of a demulsifier mixture composed of alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins in alkylbenzenes (TOLAD® 286).

F) 6 parts of an aromatic solvent with a boiling range of 196-256°C and a viscosity of 1.7 cSt at 25°C.

G) 0.5 part of tetrapropenyl succinic acid, supplied as a 50% solution in light mineral oil.

This concentrate is blended with gasoline at a concentration of 0.43 kg/m³ (150 pounds per thousand barrels (ptb)).

EXAMPLE 5

Example 4 is repeated using each of the components set forth therein except that 0.515 kg/m³ (180 ptb) of the additive concentrate is formulated with gasoline.

EXAMPLE 6

Example 4 is repeated using each of the components set forth therein except that 0.644 kg/m³ (225 ptb) of the additive concentrate is used in the gasoline mixture.

EXAMPLE 7

A fuel additive concentrate is prepared from the following ingredients:

A) 60 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride having an acid number of 1.1 (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 950) with a commercial mixture approximating triethylene tetramine, in a mole ratio of 2:1 respectively.

B) 140 parts of polyoxyalkylene compound having an average molecular weight in the range of from about 1500 to about 2000.

C) 14 parts of methylcyclopentadienyl manganese tricarbonyl.

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D) 2 parts of a tertiary butylated phenol antioxidant mixture containing a minimum of 75 percent of 2,6-di-tert-butylphenol, 10-15 percent of 2,4,6-tri-tert-butylphenol, and 15-10 percent of 2-tert-butylphenol.

E) 3.4 parts of a demulsifier mixture composed of polyoxyalkylene glycols and oxyalkylated alkylphenolic resins in alkylbenzenes (TOLAD® 9308).

F) 48 parts of Aromatic 150 solvent.

This concentrate is blended with gasolines and with diesel fuels at concentrations of 0.715 kg/m³ (250 pounds per thousand barrels).

EXAMPLE 8

A fuel additive concentrate is prepared from the following ingredients:

A) 135 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride having an acid number of 1.1 (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 950) with a commercial mixture approximating triethylene tetramine, in a mole ratio of 2:1 respectively.

B1) 135 parts of naphthenic mineral oil of Witco Corporation 4053-Heavy.

B2) 67.5 parts of 10 cSt hydrotreated PAO formed by oligomerization of 1-decene, and catalytic hydrogenation of the oligomer.

B3) 67.5 parts of polyoxyalkylene compound (Polyglycol 1200; Dow Chemical Co.)

C) 31.5 parts of methylcyclopentadienyl manganese tricarbonyl.

D) 30 parts of a mixture of 15 parts of N,N'-di-sec-butyl-p-phenylenediamine and 15 parts of a tertiary butylated phenol antioxidant mixture containing a minimum of 75 percent of 2,6-di-tert-butylphenol, 10-15 percent of 2,4,6-tri-tert-butylphenol, and 15-10 percent of 2-tert-butylphenol.

E) 10 parts of a demulsifier mixture composed of alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins in alkylbenzenes (TOLAD® 286K).

F) 120 parts of an aromatic solvent with a boiling range of 196-256°C and a viscosity of 1.7 cSt at 25°C.

G) 5 parts of aspartic acid, N-(3-carboxy-1-oxo-2-propenyl)-N-octadecyl-bis(2-methylpropyl) ester.

This concentrate is blended with gasolines and with diesel fuels at concentrations of 400, 800, 1200 and 2000 ppm.

EXAMPLE 9

Example 8 is repeated except that component G) is omitted.

EXAMPLE 10

Example 8 is repeated using each of the components set forth therein except that 150 parts of component A) and 105 parts of component F) are used.

EXAMPLE 11

Example 8 is repeated using as component A) 135 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 750) and an acid number of 1.2 with triethylene tetramine in a mole ratio of 1.8 : 1 respectively.

EXAMPLE 12

Example 8 is repeated using as component A) 135 parts of a detergent/dispersant formed by reacting polyisobutenylsuccinic anhydride with an acid number of 1.0 (made by reaction of maleic anhydride and polyisobutene having a number average molecular weight of 1200) with triethylene tetramine in a mole ratio of 2.2 : 1 respectively.

EXAMPLE 13

Example 8 is repeated with the following changes: Component A) is 170 parts of the detergent/dispersant admixed with 520 parts of 500 Solvent Neutral Oil, the acid number of the polyisobutenylsuccinic anhydride used in making the detergent dispersant is 0.9.

Claims

1. Use in a fuel composition of a combination of

- 5 i) at least one fuel-soluble detergent/dispersant selected from (a) fuel-soluble imides of long chain aliphatic hydrocarbon-substituted dicarboxylic acids or their anhydrides, (b) long chain aliphatic hydrocarbons having a polyamine attached directly thereto and (c) Mannich condensation products formed by condensing a long chain aliphatic hydrocarbon-substituted phenol with an aldehyde, and an amine; wherein the long chain hydrocarbon group in (a), (b) and (c) is a polymer of at least one C₂ to C₁₀ monoolefin, the polymer having a number average molecular weight of at least about 300;
- 10 ii) at least one fuel-soluble cyclopentadienyl complex of a transition metal; and
- iii) at least one fuel-soluble liquid carrier,

for controlling intake valve deposits in internal combustion engines operated on gasoline.

2. Use according to claim 1 wherein the long chain hydrocarbon group in (a), (b) and (c) is a polymer of at least one C₃ or C₄ monoolefin, and wherein the number average molecular weight is at least about 700.

3. Use according to claim 1 or 2 wherein the detergent/dispersant is a succinimide of a hydrocarbyl polyamine or of a polyoxyalkylene polyamine.

4. Use according to claim 3 wherein the detergent/dispersant is a polyisobutenyl polyamine.

5. Use according to claim 1 wherein the detergent/dispersant is a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound in which the alkyl group has a number average molecular weight of from 600 to 3000, (2) a polyamine which contains an amino group having at least one active hydrogen atom, and (3) formaldehyde or a formaldehyde-formed reagent, the molar ratio of reactants (1):(2):(3) being 1: 0.1-10:0.1-10.

6. Use according to any one of claims 1 to 5 wherein the transition metal is iron or manganese.

7. Use according to any one of claims 1 to 6 wherein the liquid carrier is selected from:

- 35 1) a mineral oil having a viscosity index of less than about 90 and a volatility of 50% or less as determined by the test method described in the specification hereof;
- 2) a hydrotreated or unhydrotreated poly- α -olefin oligomer having a volatility of 50% or less as determined by the test method described in the specification hereof;
- 3) a polyoxyalkylene compound having a molecular weight of greater than about 1500;
- 4) a paraffinic base mineral oil having a viscosity of 65 cSt (300 SUS) at 40°C to 150 cSt (700 SUS) at 40°C; and
- 40 5) a mixture of any two or any three or all four of 1), 2), 3) and 4).

8. Use according to any one of claims 1 to 7 in which the fuel composition further comprises a minor but effective amount of one or more of:

- 45 a) at least one fuel-soluble antioxidant;
- b) at least one fuel-soluble demulsifier;
- c) at least one fuel-soluble rust or corrosion inhibitor;
- d) metal deactivators; or
- 50 e) marker dyes.

Patentansprüche

1. Verwendung einer Kombination aus

- 55 i) mindestens einem in Brennstoff löslichen Detergenz/Dispergiermittel ausgewählt unter (a) in Brennstoff löslichen Imiden von mit langkettigen aliphatischen Kohlenwasserstoffen substituierten Dicarbonsäuren oder deren Anhydriden, (b) langkettigen, aliphatischen Kohlenwasserstoffen mit einem direkt daran gebundenen Po-

lyamin und (c) Mannich-Kondensationsprodukten, die durch Kondensation eines mit einem langkettigen aliphatischen Kohlenwasserstoff substituierten Phenols mit einem Aldehyd und einem Amin gebildet wurden, wobei die langkettige Kohlenwasserstoffgruppe in (a), (b) und (c) ein Polymer von mindestens einem C₂-C₁₀-Monoolefin ist, das ein Molekulargewichtszahlenmittel von mindestens etwa 300 aufweist,
 5 ii) mindestens einem in Brennstoff löslichen Cyclopentadienylkomplex eines Übergangsmetalls, und
 iii) mindestens einem in Brennstoff löslichen, flüssigen Träger,

in einer Brennstoffzusammensetzung zur Steuerung von Ablagerungen auf Einlaßventilen in mit Kraftstoff betriebenen Verbrennungsmotoren.

2. Verwendung nach Anspruch 1, wobei die langkettige Kohlenwasserstoffgruppe in (a), (b) und (c) ein Polymer aus mindestens einem C₃- oder C₄-Monoolefin ist und wobei das Molekulargewichtszahlenmittel mindestens etwa 700 beträgt.
3. Verwendung nach Anspruch 1 oder 2, wobei das Detergenz/Dispergiermittel ein Succinimid eines Hydrocarbylpolyamins oder eines Polyoxyalkylenpolyamins ist.
4. Verwendung nach Anspruch 3, wobei das Detergenz/Dispergiermittel ein Polyisobutenylpolyamin ist.
5. Verwendung nach Anspruch 1, wobei das Detergenz/Dispergiermittel ein Kondensationsprodukt von (1) einer schwefelfreien, Alkyl-substituierten, aromatischen Hydroxyverbindung mit hohem Molekulargewicht, in der die Alkylgruppe ein Molekulargewichtszahlenmittel von 600 bis 3000 aufweist, (2) einem Polyamin, das eine Amino-
 20 gruppe mit mindestens einem aktiven Wasserstoffatom enthält, und (3) Formaldehyd oder einem Formaldehyd bildenden Reagenz ist, wobei das Molverhältnis der Reaktanten (1):(2):(3) 1:0,1 - 10:0,1 - 10 beträgt.
6. Verwendung nach einem der Ansprüche 1 bis 5, wobei das Übergangsmetall Eisen oder Mangan ist.
7. Verwendung nach einem der Ansprüche 1 bis 6, wobei der flüssige Träger ausgewählt ist unter:
 - 1) einem Mineralöl mit einem Viskositätsindex von unter etwa 90 und einer Flüchtigkeit von 50 % oder weniger, bestimmt anhand der in der Beschreibung erläuterten Testmethode,
 - 2) einem gegebenenfalls katalytisch hydrierten Poly- α -olefinoligomer mit einer Flüchtigkeit von 50 % oder weniger, bestimmt anhand der in der Beschreibung erläuterten Testmethode,
 - 3) einer Polyoxyalkylenverbindung mit einem Molekulargewicht von über etwa 1500,
 - 35 4) einem Mineralöl auf Paraffinbasis mit einer Viskosität von 65 cSt (300 SUS) bei 40 °C bis 150 cSt (700 SUS) bei 40 °C, und
 - 5) einem Gemisch von jeweils zwei oder drei oder allen vier von 1), 2), 3) und 4).
8. Verwendung nach einem der Ansprüche 1 bis 7, wobei die Brennstoffzusammensetzung weiter eine kleinere, jedoch wirksame Menge von einem oder mehreren enthält von:
 - a) mindestens einem in Brennstoff löslichen Antioxidationsmittel,
 - b) mindestens einem in Brennstoff löslichen Demulgiermittel,
 - c) mindestens einem in Brennstoff löslichen Rost- oder Korrosionsinhibitor,
 - 45 d) Metalldesaktivatoren, oder
 - e) Farbstoffen zur Markierung.

Revendications

1. Utilisation dans une composition de carburant d'une association

i) d'au moins un détergent/dispersant, soluble dans les carburants, choisi entre (a) des imides, solubles dans les carburants, d'acides di-carboxyliques à substituants hydrocarbonés aliphatiques à chaîne longue ou de leurs anhydrides, (b) des hydrocarbures aliphatiques à chaîne longue comportant une polyamine fixée directement à ces hydrocarbures, et (c) des produits de condensation de Mannich formés en condensant un phénol à substituant hydrocarboné aliphatique à chaîne longue avec un aldéhyde, et une amine ; dans laquelle le groupe hydrocarboné à chaîne longue en (a), (b) et (c) est un polymère d'au moins une mono-oléfine en C₂

à C₁₀, polymère qui a une moyenne numérique du poids moléculaire d'au moins environ 300 ;
 ii) d'au moins un complexe cyclopentadiénylique d'un métal de transition, soluble dans les carburants ; et
 iii) d'au moins un véhicule liquide, soluble dans les carburants, pour limiter les dépôts sur les soupapes d'admission dans des moteurs à combustion interne fonctionnant à l'essence.

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2. Utilisation suivant la revendication 1, dans laquelle le groupe hydrocarboné à chaîne longue en (a), (b) et (c) est un polymère d'au moins une mono-oléfine en C₃ ou C₄, et dans laquelle la moyenne numérique du poids moléculaire est égale à au moins environ 700.

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3. Utilisation suivant la revendication 1 ou 2, dans laquelle le détergent/dispersant est un succinimide d'une hydrocarbylepolyamine ou d'une polyoxyalkylènepolyamine.

4. Utilisation suivant la revendication 3, dans laquelle le détergent/dispersant est une polyisobuténylamine.

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5. Utilisation suivant la revendication 1, dans laquelle le détergent/dispersant est un produit de condensation (1) d'un composé hydroxyaromatique à substituant alkyle, dépourvu de soufre, de haut poids moléculaire dans lequel le groupe alkyle a une moyenne numérique du poids moléculaire de 600 à 3000, (2) d'une polyamine qui contient un groupe amino ayant au moins un atome d'hydrogène actif, et (3) de formaldéhyde ou d'un réactif donnant du formaldéhyde, le rapport molaire des corps réactionnels (1):(2):(3) étant compris dans l'intervalle de 1:0,1-10:0,1-10.

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6. Utilisation suivant l'une quelconque des revendications 1 à 5, dans laquelle le métal de transition est le fer ou le manganèse.

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7. Utilisation suivant l'une quelconque des revendications 1 à 6, dans laquelle le véhicule liquide est choisi entre :

1) une huile minérale ayant un indice de viscosité inférieur à environ 90 et une volatilité égale ou inférieure à 50 %, déterminée par la méthode d'essai décrite dans la description de la présente invention ;

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2) un oligomère poly- α -oléfinique hydrotraité ou non hydrotraité ayant une volatilité égale ou inférieure à 50 %, déterminée par la méthode d'essai décrite dans la description de la présente invention ;

3) un composé de polyoxyalkylène ayant un poids moléculaire supérieur à environ 1500 ;

4) une huile minérale de base paraffinique ayant une viscosité de 65 cSt (300 SUS) à 40°C à 150 cSt (700 SUS) à 40°C ; et

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5) un mélange de deux quelconques ou trois quelconques ou bien de l'ensemble des quatre constituants 1), 2), 3) et 4).

8. Utilisation suivant l'une quelconque des revendications 1 à 7, dans laquelle la composition de carburant comprend en outre une quantité petite mais efficace d'un ou plusieurs des constituants suivants :

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a) au moins un anti-oxydant soluble dans les carburants ;

b) au moins un désémulsionnant soluble dans les carburants ;

c) au moins un additif anti-rouille ou inhibiteur de corrosion soluble dans les carburants ;

d) des désactivateurs de métaux ;

e) des colorants servant de marqueurs.

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